63-4-1

MICROWAVE AND MASS SPECTRA OF S_2F_2 [1]

Sir:

The preparation of sulfur monofluoride (S_2F_2) has been claimed by a number of investigators.[2-5] More recently an infrared spectrum was assigned to this species.[6] However, doubts have been expressed about the characterization[7,8] and existence of S_2F_2.[9] Using methods similar to those of the earlier workers, we have prepared S_2F_2 and have positively identified it as S_2F_2 by means of its mass and microwave spectra. We further determined the structure which turns out to be an analogue of the well known SOF_2.

Approximately 1g of argentous fluoride (AgF) and 6g of sulfur were mixed and slowly heated in vacuo in glass to the melting point of sulfur. The gases produced were condensed with liquid N_2. Microwave absorption lines were observed due to SO_2 and SOF_2 as well as additional lines. The mass spectrum indicated SiF_4, SO_2 and SOF_2 as well as peaks at 83 and 102 m/e units. The analysis of the mass spectrum, taking into account the presence of SiF_4, SO_2 and SOF_2 and the expected isotopic contributions from sulfur led to the tentative conclusion that the new microwave lines were due to S_2F_2.

Drying of AgF in vacuum reduced the SO_2, SiF_4 and SOF_2 content and increased the S_2F_2 yield. It also brought in microwave and mass peaks due to SF_4. Low temperature fractional distillation produced a sample which we estimate contained approximately 90% S_2F_2 with SO_2, SOF_2, SF_4 as impurities. The relative mass spectral cracking pattern obtained after correction for SO_2, SOF_2 and SF_4 is reported in Table I.

The microwave spectrum of S_2F_2 was observed and assigned to transitions, largely with the aid of the Stark patterns and the fit to a rigid rotor formula. See Table II. In addition to the spectrum of the main species, weaker satellite lines were found which had approximately the correct relative intensity to be sulfur 34 lines and the correct temperature dependence of intensity. See also Table II. Table III shows the rotational constants and moments of inertia extracted from the analyzed spectra. These were used to determine the structure of S_2F_2, applying several alternative standard methods. The bond distances and angles shown in Figure 1 carry limits of error which generously cover the variations among these methods.

This structure is very similar to that of SOF_2 in which[10] the sulfur fluorine distance is 1.58Å, angle FSF 92.8° and angle FSO 106.8°. The sulfur-sulfur distance in S_2 is reported[11] to be 1.89Å.

The basis for asserting that the above microwave spectrum is due to S_2F_2 is as follows. 1) The intensity of these microwave lines obtained from different samples with different purification steps correlate with mass spectral analysis indicating the amount of S_2F_2. 2) The structure obtained by assuming that the empirical composition is S_2F_2 is almost identical with that predicted from the known structure of SOF_2. 3) The microwave data alone and the moments of inertia obtained therefrom are only reasonable for S_2F_2, for from this data one can show that the molecule contains at least two nonequivalent atoms of sulfur, that it does not contain any other elements which have two or more isotopic species in

appreciable abundance, that it is nonplaner and therefore has more than three atoms, that the two sulfur atoms lie in a plane of symmetry so that there is at least one equivalent pair of other atoms out of this plane, and finally that the molecule is almost certainly S_2F_2 because other choices lead to interatomic parameters which would conflict either with known ranges of non-bonded distances or known ranges of bonded distances.

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Table I

RELATIVE MASS SPECTRAL CRACKING PATTERN FOR S_2F_2[a]

M/charge	Relative Abundance	Assignment
102	100	$S_2F_2^+$
83	30.2	S_2F^+
70	7.4	SF_2^+
64	23.2	S_2^+
51	6.6	$SF^+(S_2F_2^{++})$
32	26.6	$S^+(S_2^{++})$
19	2.6	F^+
41.5	~0.6	S_2F^{++}
35	<0.1	SF_2^{++}

[a] Obtained with Consolidated Engineering Corporation Spectrometer Model 21-103c at 70 ionizing volts and 10 μa ionizing current.

Table II

MICROWAVE SPECTRUM OF S_2F_2 [a]

Transition	Obs.	Calc.
	$S^{32}\ S^{32}\ F_2$	
$0_{00} \rightarrow 1_{10}$	12147.40	12147.27
$1_{01} \rightarrow 2_{11}$	20083.62	20083.57
$1_{10} \rightarrow 2_{11}$	14937.61	(14937.61)[b]
$1_{11} \rightarrow 2_{12}$	13067.63	(13067.63)
$2_{12} \rightarrow 2_{20}$	15577.32	15576.99
$1_{11} \rightarrow 2_{21}$	28505.50	(28505.50)
$2_{11} \rightarrow 3_{21}$	34312.85	34313.12
$3_{22} \rightarrow 3_{30}$	23486.60	23486.75
$4_{23} \rightarrow 4_{31}$	23915.70	23916.24
	$S^{32}\ S^{34}\ F_2$	
$0_{00} \rightarrow 1_{10}$	12068.54	(12068.54)
$1_{01} \rightarrow 2_{11}$	19969.03	(19969.03)
$1_{11} \rightarrow 2_{21}$	28304.60	28305.14
$2_{12} \rightarrow 3_{22}$	36205.45	36205.62
$2_{11} \rightarrow 3_{21}$	34109.39	34108.86
$3_{22} \rightarrow 3_{30}$	23230.90	(23230.90)
	$S^{34}\ S^{32}\ F_2$	
$0_{00} \rightarrow 1_{10}$	12007.65	(12007.65)
$1_{01} \rightarrow 2_{11}$	19676.66	(19676.66)
$1_{11} \rightarrow 2_{21}$	28353.30	28353.95
$3_{22} \rightarrow 3_{30}$	23972.04	(23972.03)
$4_{23} \rightarrow 4_{31}$	24341.36	24340.95

[a] Obtained with a conventional Stark modulated spectrometer. Frequencies reproducible to ± 0.1 Mc.

[b] Transitions in parenthesis used to calculate rotational constants.

Table III

ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR S_2F_2

	$S^{32}S^{32}F_2$	$S^{32}S^{34}F_2$	$S^{34}S^{32}F_2$
A	8179.12±0.1 Mc	8118.30±0.2 Mc	8173.15±0.2 Mc
B	3968.15±0.1	3950.24±0.1	3834.50±0.1
C	3033.16±0.1	3030.90±0.4	2955.48±0.4
I_A	61.8075±0.001C AmuÅ^2	62.2705±0.0016 AmuÅ^2	61.8527±0.0016 AmuÅ^2
I_B	127.3971 ±0.0030	127.9748 ± 0.0030	131.8375 ± 0.0030
I_C	166.6681 ± 0.0055	166.7989 ± 0.0300	171.0556 ± 0.0300
$I_A+I_C-I_B$	101.0785 ± 0.0095	101.0946 ± 0.0346	101.0708 ± 0.0346

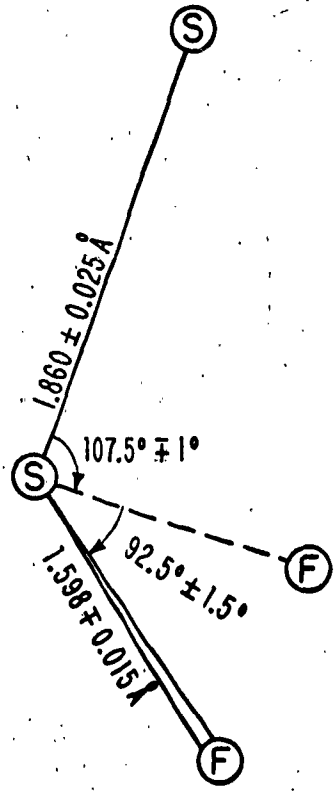

Fig. 1 Structure of S_2F_2.